

# Magnetic properties of Cu-doped porous silica gels: A possible Cu ferromagnet

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(Received 27 July 1992; revised manuscript received 9 September 1992)

We have studied the magnetic properties of Cu-doped porous silica gels and found that the system seems to be ferromagnetic up to room temperature. This result is fascinating because the amount of Cu ranges from 0.15% to 3% in weight of the total sample. Magnetization, hysteresis loops, and EPR experiments are presented. The paramagnetic signal of the silica gel without doping is negligible. On the other hand, the analysis of the magnetic impurities by x-ray fluorescence shows that these impurities can account for only 10% of the magnetization observed at 300 K.

The field of new magnetic materials is actively growing due to its importance in technological applications and its basic physical properties.<sup>1-3</sup> The growth is specially relevant for very small systems such as small magnetic particles,<sup>2</sup> thin magnetic films,<sup>3</sup> nanocrystals,<sup>4</sup> and diluted magnetic systems.<sup>5</sup> In this paper the magnetic properties of Cu incorporated in porous silica gels are summarized. It was found that when small amounts of Cu (of the order of a few wt. %) are introduced in the disordered and low-density insulating matrix the samples become ferromagnetic after heating and baking up to 700–1000 K. Such behavior was found from magnetic susceptibility and EPR experiments. The first data showed hysteresis loops as well as constant magnetization with temperature up to 300 K, the maximum temperature that can be reached in our magnetometer. EPR experiments showed that, depending on the heat treatment, the Cu<sup>2+</sup> changes its environment in the matrix. For samples that have been treated up to 900 K the paramagnetic signal disappears. The content of magnetic impurities has been analyzed by x-ray fluorescence; their maximum contribution to the magnetic moment should be about 10% of that experimentally observed at 300 K. It appears likely that the Cu<sup>2+</sup> ions couple ferromagnetically and some possible explanations have been made.<sup>6-9</sup>

Low-frequency Raman scattering and thermoporometry<sup>10</sup> indicate that silica gels present a porous structure with a high ratio of surface to volume due to large cavities and a different grain distribution. The study of these composites is a subject of increasing interest in catalysis, optics, and electronics.<sup>11-14</sup> Magnetic properties can show interesting effects because it may be possible to form very small clusters of magnetic material (even if the dopant is nonferromagnetic in bulk crystal

form as, for example, Cu) that in turn may couple with each other. The magnetic order within the metallic clusters as well as the intercluster interactions are expected to be determined by the insulating and topologically highly disordered nature of the matrix. In particular the insulating characteristic of the gel should give rise to noticeable differences from the better known magnetic behavior of systems consisting of magnetic atoms, or clusters, diluted in a metallic medium.<sup>15,16</sup> To investigate this, samples with Cu as dopant of a silica gel were prepared. In order to characterize the magnetic properties, magnetization and dc magnetic susceptibility measurements as well as EPR experiments have been performed.

The samples have been prepared, following Ref. 11, by the sol-gel process<sup>11</sup> that has been already used to obtain different diphasic ceramic-metal materials. The starting materials were tetraethylorthosilicate (TEOS) and CuCl. TEOS (17.74 mL) was partially hydrolyzed by dropping into a mixed solution of H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, and HCl, after the solution was stirred for 30 min. Then 0.216 g of CuCl suspended in 3.2 mL of CH<sub>3</sub>CN was added followed by stirring for 60 min at room temperature (RT). The solution was hydrolyzed by adding a mixed solution of H<sub>2</sub>O, C<sub>2</sub>H<sub>5</sub>OH, and HCl (molar ratio TEOS:H<sub>2</sub>O=5). The solution was stirred again and was poured into a polystyrene container and allowed to gelate at RT with a cover of Al foil. Gels obtained after 8 days were dried at RT for 20 days by evaporation of solvents through pinholes produced on the Al foil. Then samples were heated into a furnace and baked at different *T* up to 1000 K for 2 h and then slowly cooled. The quantities added to the samples contain 3% in weight of Cu (see discussion below).

The magnetization, dc susceptibility, and hysteresis loops were measured using a superconducting quantum

interference device magnetometer. The first measurements were performed for a sample (40 mg) that was heated up to 925 K and exhibited a green-brown color. The magnetization as well as the inverse of the susceptibility were almost constant for  $T > 50$  K. This is characteristic of an ordered ferromagnetic state. At low  $T$  the two quantities allowed a Curie law, indicating the presence of paramagnetic impurities. From the magnetization at high and low  $T$  we deduced that  $\frac{2}{3}$  of the spins are in the paramagnetic state. To confirm the existence of magnetic order we measured hysteresis loops. Clearly the system showed hysteresis at 10 and 300 K with practically the same coercive field of 15 Oe. It could be argued that the hysteresis and the magnetization were due to magnetic impurities. However, x-ray fluorescence analysis of the samples showed impurity levels that could account for only up to 10% of the observed magnetization. The qualitative analysis of the samples is given in Table I. These results imply that some very unusual and new magnetic properties were occurring in these samples.

Therefore, we decided to fabricate a series of samples under different heat treatments and study not only magnetization, susceptibility, and hysteresis loops, but also

TABLE I. X-ray fluorescence analysis of the twin samples used above. The number in parentheses near to the Fe impurity indicates the percentage of magnetic moment of these ions, if all of them were in a cluster, with respect to the total magnetization of the sample. Notice that as the amount of impurities decreases the amount of Cu also decreases.

	Nonsuprapure (green-brown color)	Suprapure (green color)	Suprapure (blue color)
Copper	30 707 ppm	1654 ppm	1569 ppm
Impurities			
Iron	23 ppm (5%)	5 ppm (10%)	1 ppm (5%)
Cobalt	Nondetected	< 300 ppb	< 200 ppb
Chromium	Nondetected	< 300 ppb	< 200 ppb
Manganese	7 ppm	< 300 ppb	< 200 ppb
Nickel	7 ppm	Nondetected	Nondetected
Zinc	Nondetected		
Calcium	68 ppm		

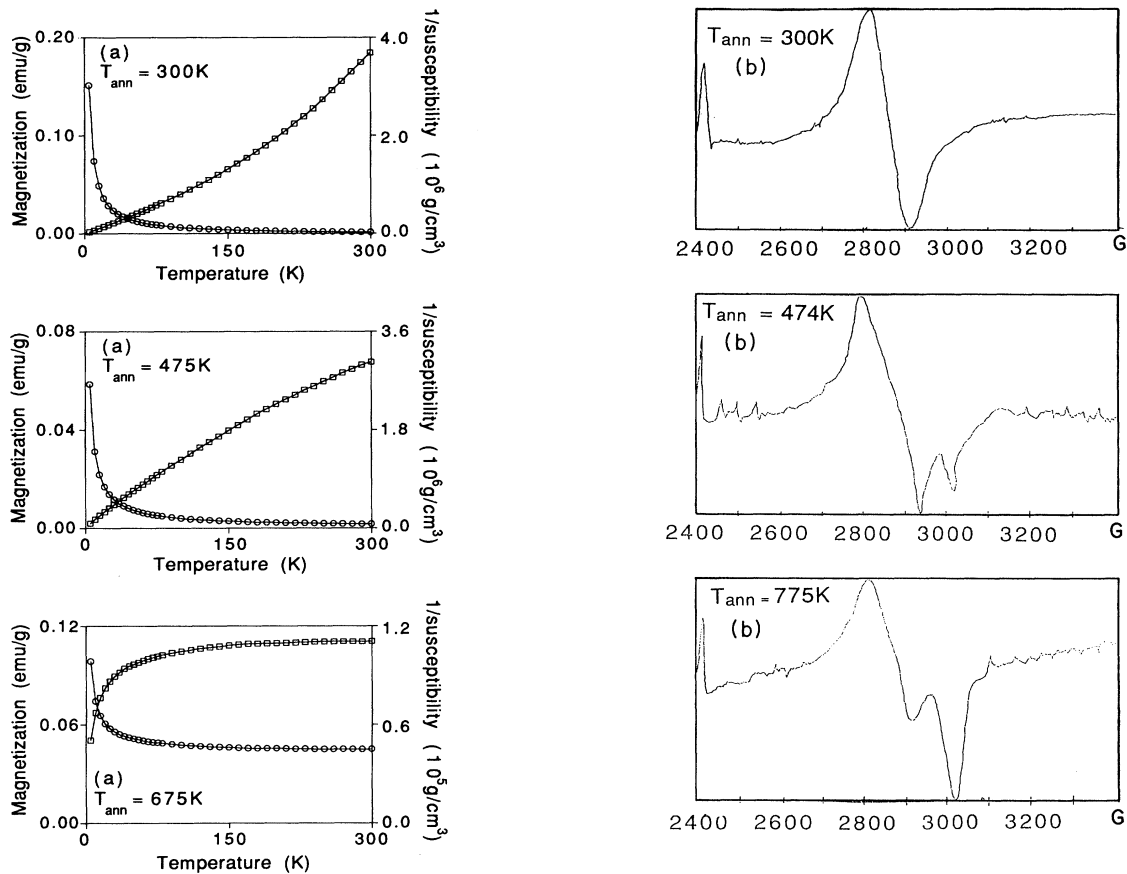


FIG. 1. (a) Temperature dependence of the magnetization ( $\circ$ ) and of the inverse of the susceptibility ( $\square$ ) for an applied magnetic field of 0.5 T and (b) EPR data for samples heated at 300, 474, and 775 K. Notice that the system becomes more ordered as the heating temperature increases. In parallel the EPR paramagnetic signal decreases as the heating temperature increases, and the satellite peak at 3000 Oe becomes larger than the one at 2880 Oe. At 925 K there is no observable EPR signal.

EPR to analyze the possible  $\text{Cu}^{2+}$  configuration.

Samples were prepared and heated at RT, 475, 675, 775, and 925 K (reported above). The magnetization results for the first three samples are presented in Fig. 1(a). The trends in magnetization and hysteresis loops indicate that for low- $T$  treatment (300 K and 475 K) the samples are paramagnetic with a reasonable Curie law and no hysteresis loop, although the one at 475 K already showed a constant magnetization at high  $T$  and a bending over of the inverse susceptibility. This is still more pronounced for the sample heated at 675 K, where the magnetization became constant at high  $T$  and exhibits a hysteresis loop with a coercive field of 20 Oe. Similar trends were shown by the EPR experiments performed at 300 K. These are presented in Fig. 1(b), in relative units, for samples heated at 300, 474, and 775 K. At RT, the derivative signal shows that the absorption is symmetric, however, as the annealing temperature increases the signal changes in two ways; first, it reduces in magnitude and second, a satellite peak appears at 3000 Oe ( $g = 2.09$ ) indicating that the  $\text{Cu}^{2+}$  environment is changing. In fact this satellite becomes much larger than the peak at 2880 Oe for the sample treated at 775 K. Finally, the samples that showed the best ferromagnetic order (925 K) do not show an EPR signal. These results seem to indicate that the EPR signal disappears because of the strong interaction between magnetic ions.

At this point, although x-ray analysis showed that the amount of magnetic impurities (20 ppm) was too low to account for the observed magnetic moment, we decided to produce suprapure samples, with a level of impurities of ppb. The samples showed blue and green colored separated regions. The measured magnetic properties are presented in Fig. 2 for samples heated at 925 K. The observations again indicate the following: (i) Magnetic order exists with much wider loops (coercive field  $\approx 70$  Oe). (ii) The magnetic moments at RT were smaller, by a factor of 10, than in previous nonsuprapure samples. Moreover, the ratio of the observed magnetic moment to the expected contribution to the magnetic moment coming from the content of magnetic impurities was larger as shown by the analysis below (see Table I). (iii) Even though the amount of  $\text{Cu}^{2+}$  was practically the same in the two colored regions the spontaneous magnetic moment of the green region was twice as large as that corresponding to the blue region. (iv) This sample does not yield an observable EPR signal at RT.

X-ray fluorescence analysis (see Table I) also showed some interesting aspects. First, the levels of magnetic impurities were in all cases too low to account for the magnetic moment observed at RT for the samples heated at 925 K. (The expected magnetic moment of the impurities should typically be 10% of the experimental moment.) Second, the samples were prepared with the same amount of Cu (3% in weight) and the amount of Cu in the final nonsuprapure sample was 3%, however, it was only 0.5% in the suprapure sample. Striking also is that, at RT, the ratio of the magnetic moment to the expected magnetic moment of the magnetic impurities (mainly Fe) is practically constant in the samples heated at 925 K. It seems as if the Fe impurities catalyzed the amount of Cu as well

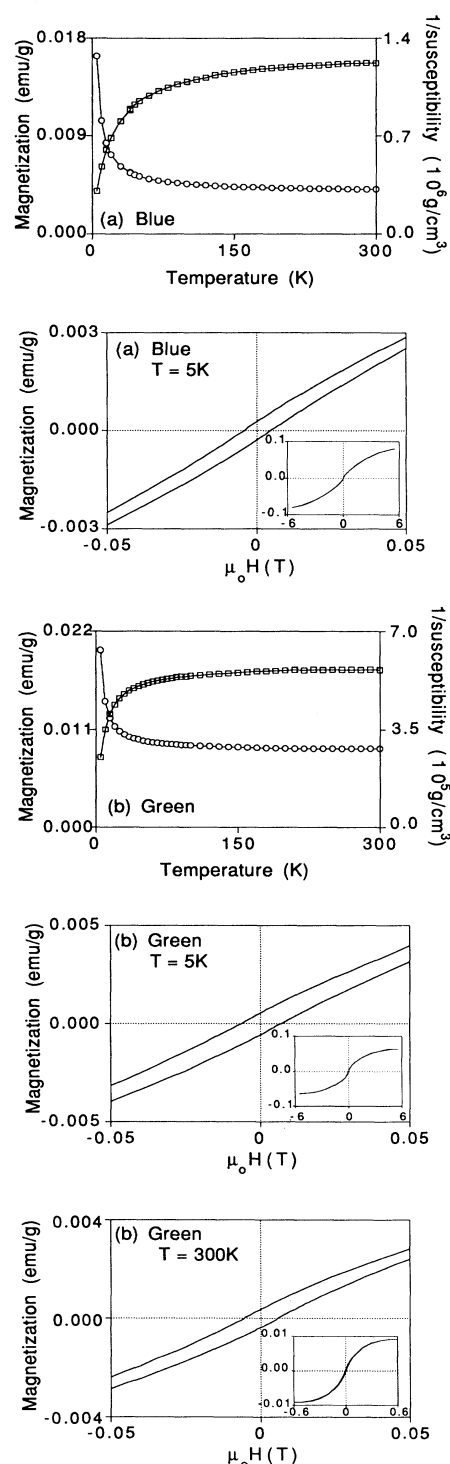


FIG. 2. Temperature dependence of the magnetization ( $\circ$ ) and of the inverse of the susceptibility ( $\square$ ) under an applied external field of 0.5 T, and hysteresis loops at  $T = 5$  K (all insets show the corresponding  $M$  vs  $H$  loops, in the same units), and also at  $T = 300$  K for the green sample, for suprapure samples for heating treatment at  $T = 925$  K for the blue (a), and the green (b), colored regions (see text). Notice the large coercive field of 60 Oe at 300 K for the green region. The Curie temperature must be at a much higher temperature.

as induced ferromagnetic order of  $\text{Cu}^{2+}$ .

We would like to offer some possible explanations. It is clear that given the amount of ordered  $\text{Cu}^{2+}$  and by assuming it to be homogeneously distributed, the distance between the  $\text{Cu}^{2+}$  would be as much as 3 nm, which is too long to invoke any kind of exchange coupling through an insulating medium. Therefore, it is reasonable to assume that the  $\text{Cu}^{2+}$  appearing in EPR at 2880 Oe diffuse, by heat treatment, in sites which nucleate in patches.<sup>15</sup> On the other hand, it is possible for the oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{2+}$  to be catalyzed by  $\text{Fe}^{3+}$  ions. As the catalytic effect has a limited radius, ferromagnetic  $\text{Cu}^{2+}$  patches can be formed around a  $\text{Fe}^{3+}$  ion. This could explain the approximate constant ratio of the magnetic moment of the sample to the magnetic moment of the magnetic impurities (mainly Fe). The ferromagnetic character of the metallic clusters could be related to the polarization of the  $d$  electrons of  $\text{Cu}^{2+}$  induced by the  $\text{Fe}^{3+}$  ions. Presumably a mechanism similar to that discussed by Bozorth *et al.*<sup>6</sup> to explain the increment of the magnetic moment of Co with Pd content, in highly diluted Co atoms in Pd, might be invoked to account for such  $\text{Cu}^{2+}$  polarization. In fact, the increment of the magnetic moment of Co atoms ranged from 1.7 Bohr units for pure Co up to 10 units in the greatest dilution (0.1 at. %), values which fit quite well to the values reported in this work. Nevertheless, the Curie temperatures of the samples reported here, for which according to Table I the Fe content is in the range 0.1–0.5 % of Cu, are found to be remarkably much higher than those corresponding to highly diluted Co in Pd (7 K). Furthermore, in pure me-

tallic metastable alloys Fe-Cu<sup>5</sup> a spin-glass-like behavior has been observed for Fe concentration below 20%. The ferromagnetic behavior of the samples reported here suggests the relevant role that might be played by the covalent disordered gel, giving rise to the appearance of  $\text{Cu}^{2+}$  ions with the magnetic moment associated to the  $d$  level.

In order to elucidate the origin of the magnetic interactions between  $\text{Fe}^{3+}$  and  $\text{Cu}^{2+}$  ions within the clusters as well as the possible interactions between clusters more experiments must be carried out.<sup>16</sup>

However, it seems clear that some of the magnetically ordered patches have dimensions above the critical superparamagnetic limit and therefore they should exhibit some anisotropy as reflected by the appearance of coercive field. By taking into account the high degree of structural disorder in the silica gel the only anisotropy we can invoke is the shape anisotropy.

In conclusion, novel ferromagnetic properties of the Cu silica gel have been reported. The Curie temperatures obtained are remarkably high and the Cu seems to be ordered as a ferromagnetic or ferrimagnet. This opens the door for development of magnetic materials where very small amounts of ions with magnetic moments give rise to high Curie temperatures.

This work has been supported by the CICYT and by the CEE through the Science program. Also we thank Dr. J. Tornero from the Servicio Interdepartamental de Fluorescencia de Rayos-X de la UAM.

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<sup>16</sup>Possible magnetic interactions between  $\text{Cu}^{2+}$  ions embedded in the matrix could be explained by direct coupling of  $\text{Cu}^{2+}$ , by tunneling (Ref. 8) in the insulating or semiconducting porous matrix, or by hybridization of the three-dimensional energy level of the  $\text{Cu}^{2+}$  ion with the empty  $s$  band of the silica, which would give rise to a higher extension of the wave function of the magnetic electron and therefore an increasing overlapping between them. Such interactions could give rise to some kind of coupling between metallic patches. See M. A. Ivanov and Y. G. Pogorelov, *Zh. Eksp. Teor. Fiz.* **88**, 1738 (1985) [*Sov. Phys. JETP* **61**, 1033 (1985)].